OXIDATION AND REDUCTION (9.1)

Oxidation - loss of electrons

Reduction - gain of electrons

Oxidation - reduction reactions (redox): the chemical changes that occur when electrons are transferred between reactants

- Oxidation reactions are always accompanied by a reduction reaction and they happen at the same time

- LEO the lion says GER!

- **L**oss **E**lectrons = **O**xidation
- **G**ain **E**lectrons = **R**eduction

- REDUCING AGENT = The substance that donates electrons in a redox reaction
  = the element or compound that is oxidized!

- OXIDIZING AGENT = The substance that takes electrons in a redox reaction
  = the element or compound that is reduced!

- to help us understand redox reactions, we split the equations up into 2 parts OR half reactions

Ex. corrosion of zinc caused by the hydrochloric acid

$Zn_{(s)} + 2HCl_{(aq)} \rightarrow ZnCl_{2(aq)} + H_{2(g)}$

Oxidation reaction : $Zn_{(s)} \rightarrow Zn^{+2}_{(aq)} + 2e^-$

Reduction reaction : $2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)}$

*Notice that the total # of electrons lost = total # of electrons gained

Writing and Balancing Half Reactions

Ex. 1 - Write a balanced net equation for the reaction of copper metal with aqueous silver nitrate

To show that the number of electrons gained equals the number lost in two half-reaction equations, it may be necessary to multiply one or both half-reaction equations by an integer to balance the electrons.

Ex. 2 - Write and label two balanced half-reaction equations to describe the reaction of zinc metal with aqueous lead(II) nitrate, as given by the following chemical equation.

Oxidation Numbers

• to be able to balance half reaction, you need to know how to find the oxidation state of an element

Oxidation Number : is a positive or negative number corresponding to the oxidation state assigned to an atom. Ex. NaCl -> Na^+, Cl^-

•it is also the charge that an atom in a molecule or ion would have if the electron pairs in covalent bonds belonged entirely to the more electronegative atom. Ex. H_2O -> oxygen is more electronegative so its oxidation number is -2 and hydrogen has an oxidation number of +1

Ex. 1 - What is the oxidation number of carbon in methane, CH_4?

Ex. 2 - What is the oxidation number of manganese in a permanganate ion, MnO_4?

Oxidation Number Changes in a Reaction

You have seen the reaction of active metals like zinc with an acid. Identify the oxidation and reduction in the reaction of zinc metal with hydrochloric acid.

BALANCING REDOX REACTION EQUATIONS (9.2)

There are two methods used for balancing REDOX equations:

Q: Balance the equation for the reaction of the permanganate ion (MnO_4^-) with the sulfite ion (SO_3^-) in a basic solution to give manganese dioxide (MnO_2) and the sulfate ion (SO_4^{2-})

OXIDATION NUMBER METHOD

a) Determine the oxidation number for each element:

$$\overset{7^+\;2^-}{MnO_4^-} + \overset{4^+\;2^-}{SO_3^{2-}} \rightarrow \overset{4^+\;2^-}{MnO_2} + \overset{6^+\;2^-}{SO_4^{2-}}$$

b) Determine the ratio of number of electrons:

c) Add water to balance any oxygen atoms:

d) Add H^+ to balance the hydrogen atoms of the water:

e) This reaction is taking place in a basic solution; add OH^- (to both sides of the equation) to balance the H^+ and cancel where needed:

HALF-REACTION (or ION ELECTRON) METHOD

A) Identify the oxidation and reduction half-reactions:

$MnO_4^- \rightarrow MnO_2$: manganese is reduced from +7 to +4

$SO_3^{2-} \rightarrow SO_4^{2-}$: sulfur is oxidized from +4 to +6

B) Add water to balance oxygen atoms:

C) Add hydrogen ions to balance the hydrogen atoms in water:

D) Add electrons to balance charges in each half-reaction:

E) Balance electrons:

F) Combine half reactions and cancel electrons, ions & molecules where necessary:

G) Add OH^- to balance the hydrogen ions (basic solution):

PREDICTING REDOX REACTIONS (9.3)

- A redox reaction can be explained as a transfer of valence electrons from 1 substance to another
- Since there are 2 particles involved, it is like a tug of war for electrons is happening between the particles
- If 1 particle can pull harder than the other, a spontaneous reaction happens. If not, no reaction happens

How to Predict What Happens

- Half-cell potentials or the relative strengths of oxidizing agent and reducing agents can be used to predict if an oxidation-reduction reaction will occur

- Spontaneity rule: if the oxidizing agent is above the reducing agent in a Table of Relative Strengths of Oxidizing and Reducing Agents (C11), the reaction will proceed

- Or ….. if the cell voltage for the over-all reaction is positive, the reaction will proceed as written

QUESTION:

Is the following reaction spontaneous?

$$Cr\ (s) + 3\ Ag^{+}\ (aq) \rightarrow Cr^{3+}\ (aq) + 3Ag\ (s)$$

SOLUTION:

- In solving these problems, identify the substance that is being reduced – THE OXIDIZING AGENT (**OA**) and the substance being oxidized – THE REDUCING AGENT (**RA**)

- Reduction half-reaction equations are read from left to right (following the forward arrow) in Table C11
- Oxidation half-reaction equations are read from right to left (following the reverse arrow) in Table C11
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- The strongest oxidizing agent (SOA) is at the top left of the table and the strongest reducing agent (SRA) is at the bottom right of the table -> you need to pick the strongest oxidizing agent and reducing agent, if you have more than 1 OA or RA

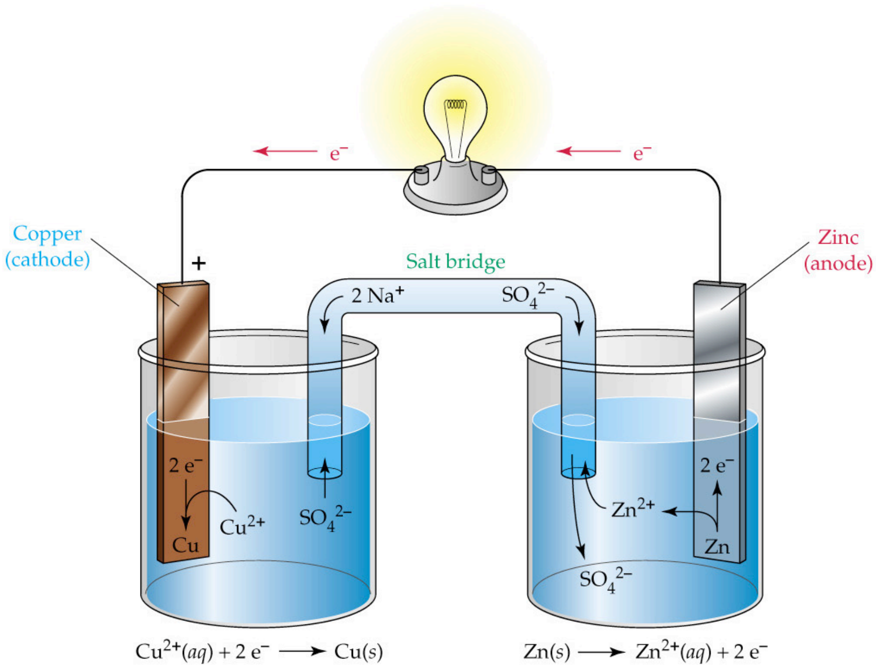
OA:

RA:

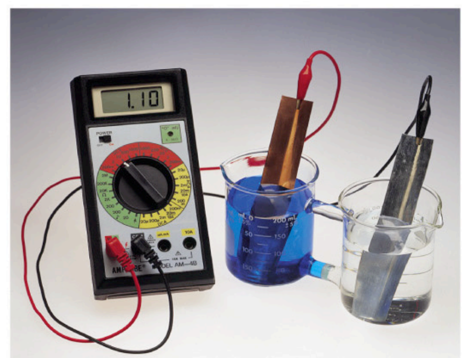
- Cell voltage (overall reaction) is a measure of how easily an oxidation – reduction will proceed
- After a time the concentration of the solutions change, as do the mass of electrodes in cells and batteries and the cell will not produce the same voltage ……… THE BATTERY DIES!
- Eventually, the system will reach equilibrium where $E^o = 0$.

GALVANIC CELLS (9.5)

- Galvanic cells or electrochemical cells are chemical systems in which there is a spontaneous oxidation-reduction reaction that produces a current of electricity



(a)



(b)

- The zinc electrode is being oxidized, producing zinc ions in solution

- Copper ions in solution are being reduced, adding copper atoms to the copper electrode

- Oxidation occurs at the anode and Reduction occurs at the cathode

- Electrons flow (externally) from the anode to the cathode

- **Salt bridge** : a salt bridge is needed to allow the movement of charges.
  -> to keep the cathode positive charged zinc ions need to be able to move to that side since the positive copper ions are being reduced to form solid copper
  ->to keep the anode negative -> the negative sulfate ions move through the salt bridge

- Electrochemical cells need enough electricity moving at an adequate rate, with sufficiently high voltage to do work

- The SI system used to measure the amount of electricity flowing through a wire is a *coulomb*: 1.04 x 10-5 mol of electrons

- The rate of flow is measured in coulombs per second or *amperes*

- *Voltage* is a measure of the tendency of the electrons to flow; the voltage of a cell measures it ability to do work

- Voltage is made up of the cell potential of the two half-reactions – oxidation and reduction

- ΔE^o: Standard Half-cell Potential : the maximum electric potential difference (voltage) of the cell operating under standard conditions -> one mole solutions at 101.3 kPa and 25°C

* the half-cell with the more positive reduction potential has a greater attraction for electrons and will gain electrons from the half-cell with the lower reduction potential

- Standard half-cell potentials are written as reduction reactions with the hydrogen half-cell as the reference ($E^o = 0$)

- These half reactions taken from Table of Relative Strengths of OA and RA:

$$Cu^{2+}_{(aq)} + 2e^- \rightarrow Cu_{(s)} \qquad E^o = +0.34\ V$$
$$\boxed{2H^+_{(aq)} + 2e^- \rightarrow H_{2(g)} \qquad E^o = 0.00\ V}$$
$$Zn^{2+}_{(aq)} + 2e^- \rightarrow Zn_{(s)} \qquad E^o = -0.76\ V$$

- Copper is the stronger oxidizing agent and more easily reduced
- Zinc is the stronger reducing agent and more easily oxidized

- To determine the potential voltage of the electrochemical cell, write the half-reactions with the corresponding voltage and add the equations

Oxidizing half-reaction:

Reduction half-reaction:

Over-all reaction:

Mathematically, the potential voltage of the cell can be determined by

$$\underset{\text{Cell}}{\Delta E^o} = \underset{\substack{\text{Cathode}\\ \text{(OA)}}}{E_r^o} - \underset{\substack{\text{Anode}\\ \text{(RA)}}}{E_r^o}$$